New Standards for Next-Generation Low-Emission Vehicles

In May 2006 NIST introduced two new gas-mixture Standard Reference Materials (SRMs) that contain significantly lower concentrations of nitric oxide (NO) in nitrogen than previously available. SRM 2737 contains a nominal NO concentration of 500 nmol/mol (ppb) and SRM 2738 contains nominally 1000 nmol/mol (ppb). Both SRMs are sold in large (30 L water volume) aluminum cylinders. The release of these SRMs concluded five years of development by NIST, with the work partially funded by the American Industry/Government Emissions Research (AIGER) consortium (U.S. Environmental Protection Agency (EPA), the California Air Resources Board (CARB), General Motors, Ford, and Daimler-Chrysler). AIGER members have identified the need for significantly lower concentration NIST gas standards containing carbon monoxide, hydrocarbons, and nitric oxide. SRMs 2737 and 2738 were identified as their highest priority.

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AIGER members are working together to facilitate the automobile industry meeting more stringent 2003 Federal Tier II and California LEV II emission regulations that go into effect over the next several years. New lower-concentration gas standards are required for emission testing of newer vehicles that produce lower levels of pollutants. The new engines employ fuel injection with air-to-fuel ratios that are optimized by on-board computers. Tailpipe emissions are further reduced by highly efficient catalytic converters.

NIST has had a long-term relationship with the AIGER group that requested that the Analytical Chemistry Division develop two new gaseous SRMs at low NO concentrations. A major roadblock to successfully developing these SRMs had been the inability of NIST's specialty gas contractors to achieve stable NO mixtures at lower SRM concentrations.

NIST became proactive in solving the stability problem resulting in a two-step successful treatment:
1) All cylinders are pretreated with an NO_2 mixture.
2) Oxygen contamination levels for dilution nitrogen are qualified by measurement at < 2 nmol/mol.

Using the above treatment, NIST developed ten stable low NO working standards ranging from 500 nmol/mol to 1250 nmol/mol. These cylinders served as the low NO benchmarks until more accurate gravimetric standards were prepared in 2005. These are the benchmarks against which the concentration values for SRMs 2737 and 2738 were assigned and against which the SRMs are being monitored for stability. Each SRM cylinder has been individually certified for NO and NO_x concentration values at an expanded uncertainty of ± 1.5% relative.

To demonstrate that analytical capabilities and results at this low level are comparable to other laboratories', NIST participated with other national metrology institutes in an international intercomparison study (CCQM-K26a NO in Nitrogen [Ambient Level]) in which each laboratory independently measured the nitric oxide concentration of a gas mixture sent by the coordinating laboratory. The Gas Metrology Group at NIST assigned a concentration of (715 ± 7) nmol/mol nitric oxide in nitrogen for the NIST test sample, referencing the suite of low-concentration NO working standards. This result was in excellent agreement with the assigned concentration value determined by the CCQM coordinating laboratory for this test sample.

Gas mixtures have been developed to meet other AIGER needs. NIST completed multiple analyses on scrubbed air and scrubbed nitrogen at the threshold of detection for CO, CO_2, SO_2, and NO_X. AIGER members submitted eight cylinders of air and eight cylinders of nitrogen that will serve as a zero reference during analytical testing. AIGER requires a known zero gas standard to establish a true zero on their analytical monitors to assist in meeting regulations. The cylinders will be shipped back to the AIGER members who ordered them.

Several AIGER members have requested that NIST blend individual gravimetric standards containing toluene, nitrous oxide, refrigerant 134b, methanol, and ammonia at a single point-of-reference concentration of 10 µmol/mol. AIGER members have purchased Innova Photoacoustic analyzers that can be calibrated using these standards. Cars are sealed into "sheds" and subjected to various environmental conditions, such as "baking." The photoacoustic analyzers are used to monitor fugitive emissions (e.g., the "new car smell," outgassing from tires) which are regulated. NIST has completed all of the standards with the exception of ammonia, which will be completed in the coming year.